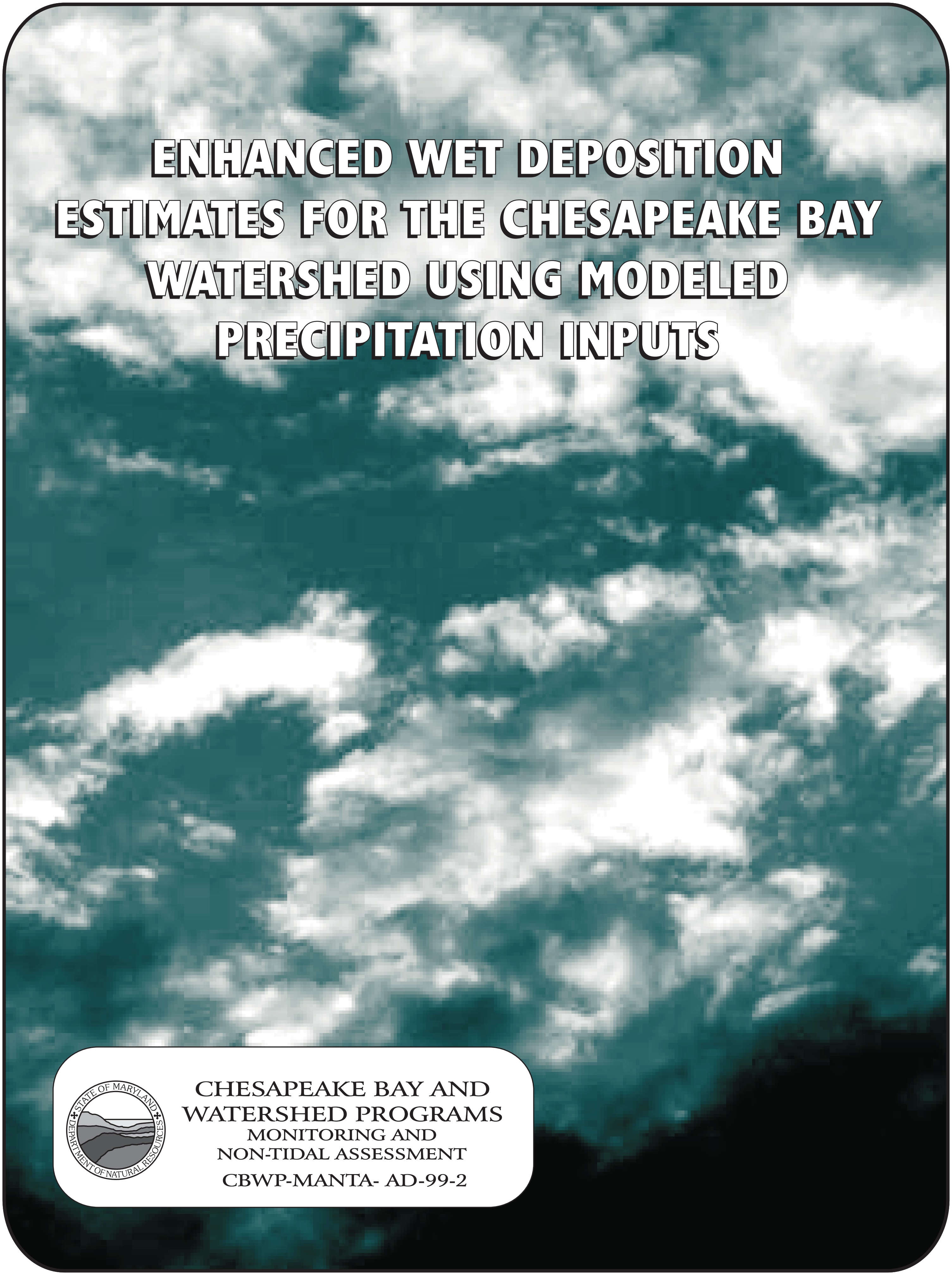


ENHANCED WET DEPOSITION ESTIMATES FOR THE CHESAPEAKE BAY WATERSHED USING MODELED PRECIPITATION INPUTS

CHESAPEAKE BAY AND
WATERSHED PROGRAMS
MONITORING AND
NON-TIDAL ASSESSMENT

CBWP-MANTA- AD-99-2

Parris N. Glendening
Governor

Kathleen K. Townsend
Lieutenant Governor

A message to Maryland's citizens

The Maryland Department of Natural Resources (DNR) seeks to preserve, protect and enhance the living resources of the state. Working in partnership with the citizens of Maryland, this worthwhile goal will become a reality. This publication provides information that will increase your understanding of how DNR strives to reach that goal through its many diverse programs.

Sarah Taylor-Rogers
Secretary

Stanley K. Arthur
Deputy Secretary

Maryland Department of Natural Resources
Tawes State Office Building
580 Taylor Avenue
Annapolis, Maryland 21401

Toll free number: 1-(877) 620 8DNR x8611
www.dnr.state.md.us

FOR FURTHER INFORMATION REGARDING THIS REPORT, PLEASE CALL 410-260-8611.
OR TOLL FREE : 1 (877) 620-8DNR x 8611

PRINTED ON RECYCLED PAPER

ENHANCED WET DEPOSITION ESTIMATES FOR THE CHESAPEAKE BAY WATERSHED USING MODELED PRECIPITATION INPUTS

Jeffrey W. Grimm
The Pennsylvania State University
Environmental Resources Research Institute
118 Land and Water Building
University Park, PA 16802

James A. Lynch
Pennsylvania State University
School of Forest Resources
311 Forest Resources Lab
University Park, PA 16802

Introduction

Atmospheric deposition is a continuous process that occurs as wet deposition (pollutants present in rain, snow, ice, fog, etc.) and dry deposition (exchange of gases, aerosols, and particles between the atmosphere and surfaces of the earth). Wet deposition is a function of the concentration of substances dissolved in precipitation or scavenged from the atmosphere during precipitation and the volume of precipitation that occurs at the point of measurement. Precipitation volumes are measured extensively throughout the United States at approximately 8,000 National Oceanic and Atmospheric Administration's (NOAA)/National Weather Service (NWS) sites (France 1994). Weekly precipitation chemistry data are available from approximately 220 sites that comprise the National Atmospheric Deposition Program(NADP)/National Trends Network(NTN) (NADP, 1999).

The amount of dry deposition that falls at a given point is a function of the atmospheric concentration of gases, aerosols, and particles and the deposition velocities at which they are deposited. Deposition velocities are difficult to measure and are highly variable, depending on the nature of the depositing substance, the nature of the surface on which they settle, and meteorological conditions. Dry deposition is monitored at relatively few sites in the United States. The largest network, EPA's Clean Air Status and Trends Network (CASTNet) measures dry deposition at 67 sites, mostly located in the eastern United States (U.S. EPA, 1999). A 6-site network (AIRMoN-Dry) is maintained by the Air Resources Lab of NOAA; these sites are also located in the eastern United States (NOAA, 1999). Because of difficulties in measuring dry deposition and the relatively sparseness of monitoring sites, direct evaluation of dry deposition patterns across the United States cannot be done. Even regional assessments are difficult because of spatial variability in emissions, deposition velocities, climate, and land cover. Consequently, most environmental assessments concerning the impact of atmospheric deposition to sensitive ecosystems are largely based on wet deposition measurements. Were total deposition is desired, dry deposition is estimated, usually as a fixed percentage of wet deposition.

The representativeness of a point estimate or multiple point estimates of wet deposition to a region or watershed, such as the Chesapeake Bay basin, and the accuracy at which these point estimates can be interpolated to unmonitored portions of the region or watershed are limiting factors in using wet atmospheric deposition measurements in environmental assessments, especially if the wet estimates are also used as a basis for estimating dry deposition. Current monitoring programs, such as the 220-site NADP/NTN, provide point estimates of wet deposition that, when combined with two-dimensional interpolation algorithms, such as the multiquadric equations algorithm (MQE) (Hardy, 1971), yield regional deposition patterns. Such numerical interpolation methods incorporate statistical functions to weight spatially limited point measurements to estimate a regularly-spaced deposition grid. Grimm and Lynch (1991) found that interpolating NADP/NTN data from Pennsylvania and neighboring states (New York, Ohio, New Jersey, West Virginia, and Maryland) to unmonitored portions of north central Pennsylvania resulted in mean percent errors for annual wet nitrate and sulfate depositions of 13%, with maximum percent errors exceeding 38%. When data from the 12-site Pennsylvania Atmospheric Deposition Monitoring Network, which used identical sampling and analytical protocols as the NADP/NTN, were included in the analysis, the mean percent and maximum percent errors were reduced to 11% and 24%, respectively. Even with the larger monitoring network, two-dimensional interpolation errors for annual wet nitrate and sulfate deposition estimates were large enough to significantly under- or over-estimate actual wet depositions in most regions of Pennsylvania (Grimm and Lynch, 1991). This was particularly true in the mountainous regions of the state where precipitation volumes are highly variable.

The major determinants of wet deposition are the volume of precipitation that falls at a given point of measurement and the concentration of dissolved substances in precipitation at that point. Topography can influence the amount of precipitation at a given point and the distribution of precipitation across a given landscape primarily by orographic uplifting of air masses which causes precipitation to increase with elevation (Sumner, 1988; Barrie, 1981; Lovett and Kinsman, 1990). Likewise, slope position and aspect also influence the amount and distribution of precipitation in a region.. It is well documented that even at the same elevation, more precipitation falls on the windward slopes of topographic barriers than on leeward slopes and adjacent valleys (Sumner, 1988; Barros and Lettenmaier, 1994). This results not only from orographic uplifting effects, but also from topographic shading. In some regions, cloud water deposition may also be an important factor (Lovett and Kinsman, 1990). Proximity to large surface waters (e.g., The Great Lakes, Atlantic Ocean) also affect the amount and distribution of rainfall in some regions of the eastern United States.

Attempts have been made to incorporate elevation as a covariate in models designed to address issues related to orographic influences on precipitation patterns in complex Terrain (Ollinger et al., 1993; Barros and Lettenmaier, 1994; Barros and Lettenmaier, 1993; Alpert and Shafir, 1989; Bell, 1978; Chaumerliac and Mahouf, 1987). Digital elevation models have also been used in hydrologic analyses and in the development of topographically-based hydrologic models (Fan and Duffy, 1991; Hornberger et al., 1985; Beven and Kirkby, 1978; Cloton, 1976; Moore et al., 1988); in ecological applications (Moore et al., 1988; Nielson, 1992); and in the estimation of atmospheric deposition in complex terrain (Jones and Choularton, 1988; Ollinger et al., 1993; Dore et al., 1992). All of these efforts have shown considerable promise because they attempt to describe the physical influence that elevation and other topographic features have on the spatial distribution of precipitation and the resultant effects of the precipitation pattern on hydrology, vegetation, and wet deposition.

The objective of this study was to develop a wet deposition model for Maryland and the Chesapeake Bay watershed that has a greater spatial resolution than is currently possible using NADP wet deposition measurements and available two-dimensional spatial interpolation algorithms. The model incorporates daily precipitation measurements from NOAA/NWS sites located within a 100 km radius of the Chesapeake Bay watershed, topographic variables (e.g., elevation, slope, aspect) that effect the amount and distribution of precipitation across the region, and precipitation chemistry data from the NADP sites within and adjacent to the region to estimate wet deposition. Because of strong coastal influence on climate in some portions of Maryland and the Chesapeake Bay watersheds, a subroutine was added to the model to correct for marine (sea-salt) influence on sulfate concentrations. The model was based on a similar model that was developed for the U.S. Forest Service as part of their Northern and Southern Global Change Research Programs (Grimm and Lynch, 1997). Model performance was tested against independent point measurements from sites located within Maryland and the Chesapeake Bay watershed. Because of the scarcity of independent point measurements in this region and the similarities between the Maryland and U.S. Forest Service Global Change models, independent measurements from three physiographic regions of the eastern United States were also included in the model performance evaluation. The performance evaluation included direct comparison of predicted and observed point estimates at the independent sites as well as a comparison of estimates based on a common two-dimensional spatial interpolation algorithm using NADP data.

Methods

A 2-Dimensional Spatial Interpolation Model

The multi quadric equations (MQE) algorithm developed by Hardy (1971) has been shown to be a suitable two-dimensional model for spatially interpolating wet atmospheric deposition estimates (Grimm and Lynch, 1991). The MQE algorithm is, therefore, used as a baseline for measuring any enhancements in estimation accuracy provided by incorporation of NOAA/NWS precipitation measurements and topographic variables, as well as, latitudinal and longitudinal information in modeling wet deposition from a given set of deposition sampling points. The surface functions of the MQE algorithm are of the form:

$$z = \sum_{I=1}^{N} h_i m_i$$

where, z = estimate value of surface at a point,
N = number of sample points,

h_i = distance between i^{th} sample point and point to be estimated, and
m_i = coefficient for i^{th} sample point.

The coefficients, m_i, for the surface functions are obtained by solving the equation series,

$$\sum_{j=1}^{N} m_i h_{ij} = z_i \qquad I=1,...,N$$

where, z_i = surface values at the i^{th} sample point, and
h_{ij} = distance between the i^{th} and j^{th} sample points.

Topographically-Enhanced Weighted Linear Least Squares Model

The topographically-enhanced model developed here is a moving neighborhood, weighted linear least squares regression algorithm (WLLSR) which yields wet deposition estimates as a function of latitude, longitude, elevation, slope, and topographic aspect, i.e.,

$$d=b_0+b_1x+b_2y+b_3xy+b_4x^2+b_5y^2+b_6e+b_7ex+b_8ey+b_9N+b_{10}S+b_{11}E+b_{12}W$$

where, d = wet deposition estimate,
x = longitudinal coordinate,
y = latitudinal coordinate,
e = elevation above sea level,
N = mean slope in northerly direction,
S = mean slope in southerly direction,
E = mean slope in easterly direction, and
W = mean slope in westerly direction.

The elevation, e, and slope/aspect parameters (N,S,E,W) were derived from 1 by 1 degree USGS digital elevation (DEM) data sets. The original 3-arc-second resolution of the DEM data sets was reduced to 6-arc-seconds (i.e., 600 rows by 600 columns per 1-degree block) to limit computer storage requirements. Each of the four slope/aspect values for a given point was determined using five, 16.1-km (10-mile) radial transects starting from the given point along bearings 0, $\pm$22.5, and $\pm$45 degrees from the major compass bearing. For example, using a value of 0 degrees for north, the transects for the northerly slope/aspect values were on bearings of 45, 22.5, 0, 337.5, and 315 degrees). A mean slope value was calculated for each transect as,

$$s=\left[\sum_{j=1}^{n_i} (e_j-e_0)/t_j\right]/n_i$$

where, s = mean slope for i^{th} transect,
n_i = number of DEM cells along i^{th} transect,
e_0 = elevation at transect origin,
e_j = elevation at j^{th} DEM cell along transect, and
t_j = distance of j^{th} DEM cell center from transect origin.

The five transect slope values were then averaged to produce the corresponding direction's slope/ aspect value for the given point.

Sample wet deposition data for both the WLLSR and MQE algorithms were derived from daily precipitation records from the National Oceanic and Atmospheric Administration's (NOAA), National Climatic Data Center and from weekly precipitation chemistry data from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). NOAA precipitation measurements are available from approximately 8,000 cooperative sites across the United States (France, 1994). In contrast, NADP/NTN precipitation chemistry data are obtainable from a relatively sparse network of approximately 220 sites across the United States (NADP, 1999). The location and relative density of NOAA precipitation monitoring sites and NADP/NTN precipitation chemistry sites are shown in Figures 1a and 1b, respectively. Because of the sparseness of NADP/ NTN sites, their data cannot be used directly to model the effects of topography on wet deposition. To obtain adequate wet deposition sample density, the concentration data from the NADP/NTN sites were interpolated using MQE to each of the NOAA sites and the corresponding concentration estimates and precipitation values were used to calculate deposition as:

$$d_i = 0.254*c_i p_i$$

where, d_i = estimated quarterly deposition (kg/ha) at the i^{th} NOAA site,
c_i = estimated quarterly concentration (mg/L) at the i^{th} NOAA site, and
p_i = measured quarterly precipitation (inches) at the i^{th} NOAA site.

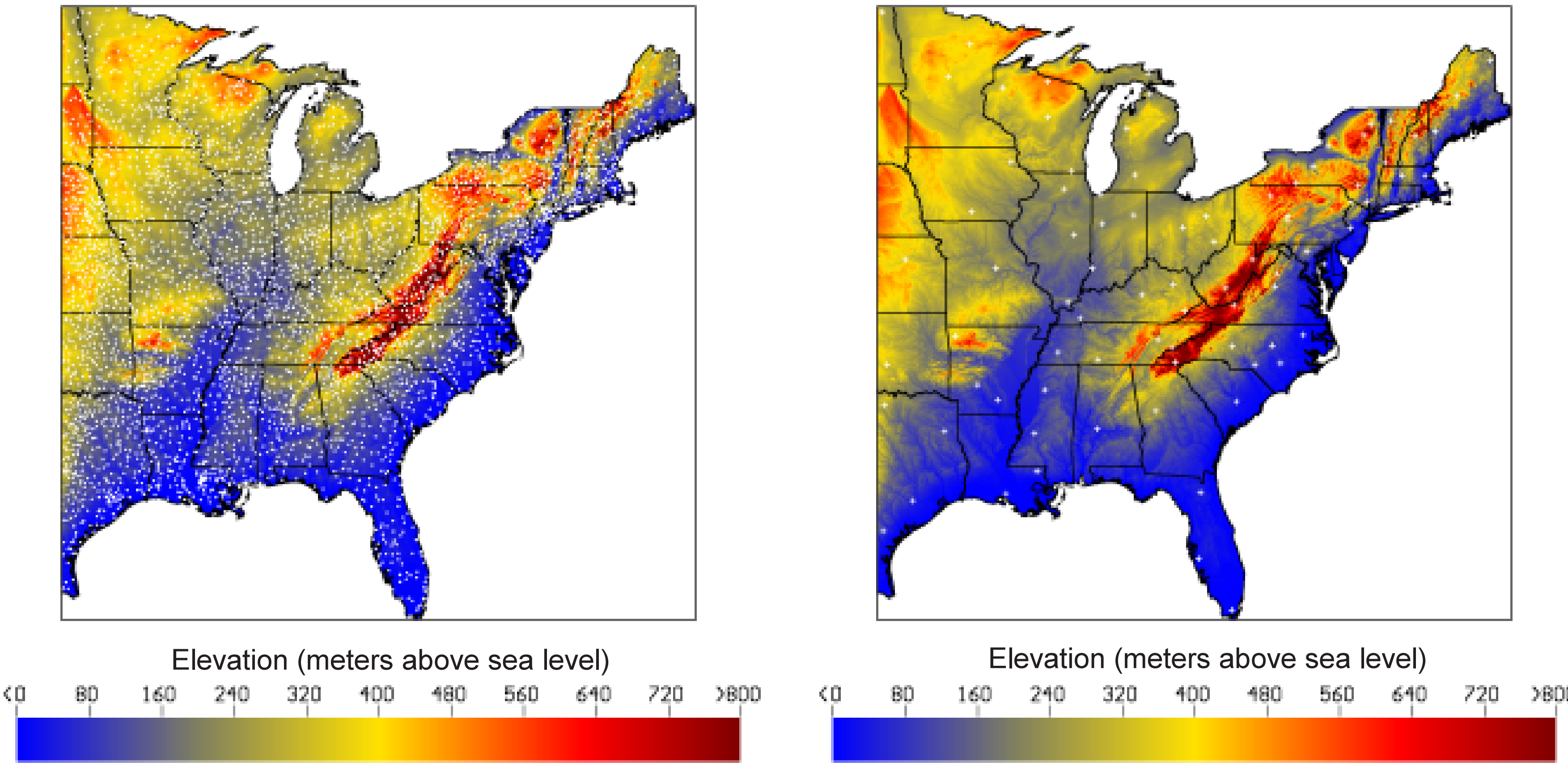
Daily precipitation and weekly concentration records were both summarized into quarters (December-February, March-May, June-August, and September-November) for each of three years from December 1989 through November 1992. Precipitation was summarized as total volume measured and precipitation ionic concentrations as volume-weighted means. Wet depositions estimates for each quarter of each year in the three-year period were modeled separately.

Observation Weighting Criteria for WLLSR

The linear model case weight assigned to a given sample value (a quarterly deposition at a given NOAA site) were determined by three functions:

Elevational balancing: The distribution of NOAA sites does not necessarily assure an even representation of the range of elevations occurring in a region. In mountainous areas, relatively few precipitation monitoring sites may be positioned at the highest elevations. To prevent different elevation strata from having uneven influence on regression solutions, the range of sample site elevations occurring within a specified radius of a point to be modeled was divided into a number of equal-length intervals, N_e. Then initial case weights were the set as follows:

$$w_{ij}=1/(n_i+3)$$



(a) (b)

Figure 1. Locations of NOAA cooperative precipitation sites (a) and National Atmospheric Deposition Program/ National Trends Network precipitation chemistry sites (b) in the Eastern United States.

where, w_{ij} = case weight for j^{th} sample value in i^{th} elevation interval,
n_i = number of sample values occurring in i^{th} elevation interval, and
N_e = number of elevation intervals.

The optimal number of elevation intervals was determined for each ion by varying the interval count from 1 to 7 and selecting the value which minimized the mean quarterly estimation error using the model performance procedure described later.

Distance weighting: The initial case weights discussed above were multiplicatively adjusted by the following factor:

for v_i v_{max}, $f_i=[1-(v_i/v_{max})^a]^b$
otherwise, $f_i=0$

where, f_i =distance weighting factor for i^{th} sample,
v_i = distance between i^{th} sample location and point to be estimated,
v_{max} = maximum radius from estimation point for inclusion of sample point in regression solution,
a = integral valued weighting exponent, and
b = integral valued weighting exponent.

Values for v_{max}, a, and b were jointly selected for each ion by their minimization of mean quarterly estimation errors. Values for v_{max} were varied from 277 to 778 km in increments of 55.6 km, which is approximately the arc-distance corresponding to one-half of a degree of latitude. Values for a and b were varied from 1 to 2 and from 1 to 9, respectively, for each value of v_{max}.

Residual weighting: The above elevation-balanced and distance-adjusted weights were used to obtain an initial weighted least squares solution. Standardized residuals (Neter and Wasserman, 1974) were calculated for each sample value and the individual case weights were multiplicatively adjusted by the following factor:

for $|u_i|$ u_{max}, $g_i=[1-(|u_i|/u_{max})^c]^d$
otherwise, $g_i=0$

where, g_i = weighting factor for i^{th} sample,
u_i = standardized residual for i^{th} sample,
u_{max} =maximum absolute value for standardized residuals for inclusion of corresponding sample in regression solution,
c = integral valued weighting exponent, and
d = integral valued weighting exponent.

As with the distance weighting factor, values for u_{max}, c, and d were jointly selected for each ion by their minimization of mean quarterly estimation errors. Values for u_{max} were varied from 2.5 to 7.0 in increments of 0.5. Values for c and d were varied from 1 to 2 and from 1 to 5, respectively, for each value of u_{max}. The resultant adjusted weights were used to obtain a final regression solution and deposition point estimates for the WLLSR algorithm.

The parameters for the three weighting functions were selected sequentially. First, the parameters for the distance weighting functions (v_{max}, a, and b) were selected by trial using five elevation intervals for the elevation balancing function and residual weighting was not performed. Then given the selected distance weighting parameters and five elevation balancing intervals, the residual weighting parameters (u_{max}, c, and d) were selected by trial. Finally, the number of elevation intervals was optimized given the selected distance and residual weighting parameters.

Model Tuning and Evaluation

The WLLSR deposition model was developed to estimate quarterly wet deposition for the portion of the U.S. east of 94 degrees west longitude. Because of the large number of NOAA sites (approximately 4,400) in this region and the large number of combinations of model weighting parameters to be screened by trial, model performance was evaluated using deposition values from all sites located in three rectangular plots situated in three distinct geographic regions of the eastern U.S. (see Figure 2):

1) Northeast region (40-43°N by 76-79°W) covers central Pennsylvania and southeastern New York states (Figure 2a). Terrain in this plot is predominantly mountainous with small portions of the northern margin and the southeastern corner consisting of rolling plains. Elevations range from 33 to 929 meters above sea level.

2) Midwest region (38-41°N by 84-87°W) covers most of Indiana and portions of western Ohio and north central Kentucky (Figure 2b). Terrain varies from glaciated plain to gently rolling hills. Elevations range from 110 to 398 meters above sea level.

3) Southeast region (33-36°N by 82-85°W) cover northern Georgia, southeastern Tennessee, and extreme western North and South Carolina (Figure 2c). This area contains the highest portions of the Smoky Mountains (Southern Appalachian Mountains). About one-third of the plot is covered by rolling hills and coastal plain. Elevations range from 0 to 2012 meters above sea level.

For each set of weighting parameters for the WLLSR model and for the MQE algorithm, model estimation accuracy was quantified. This was done by individually excluding each sample observation and fitting the model parameters using the observations from the remaining sites within the data inclusion radii. This process of estimating values for individually excluded observations was performed for each quarter from December 1989 through November 1992. Discrepancies between the excluded sample values and their values, as predicted by the WLLSR and MQE models, were then summarized into estimation error rates to evaluate model performance. Estimation errors were grouped into three individual years (December 1989 - November 1990, December 1990 - November 1991, and December 1991 - November 1992 are referred to as 1990, 1991, and 1992, respectively).

Data from only those sites not having any lapse in precipitation records within a given summary year were used in model performance evaluation. Quarterly estimation errors were summarized into

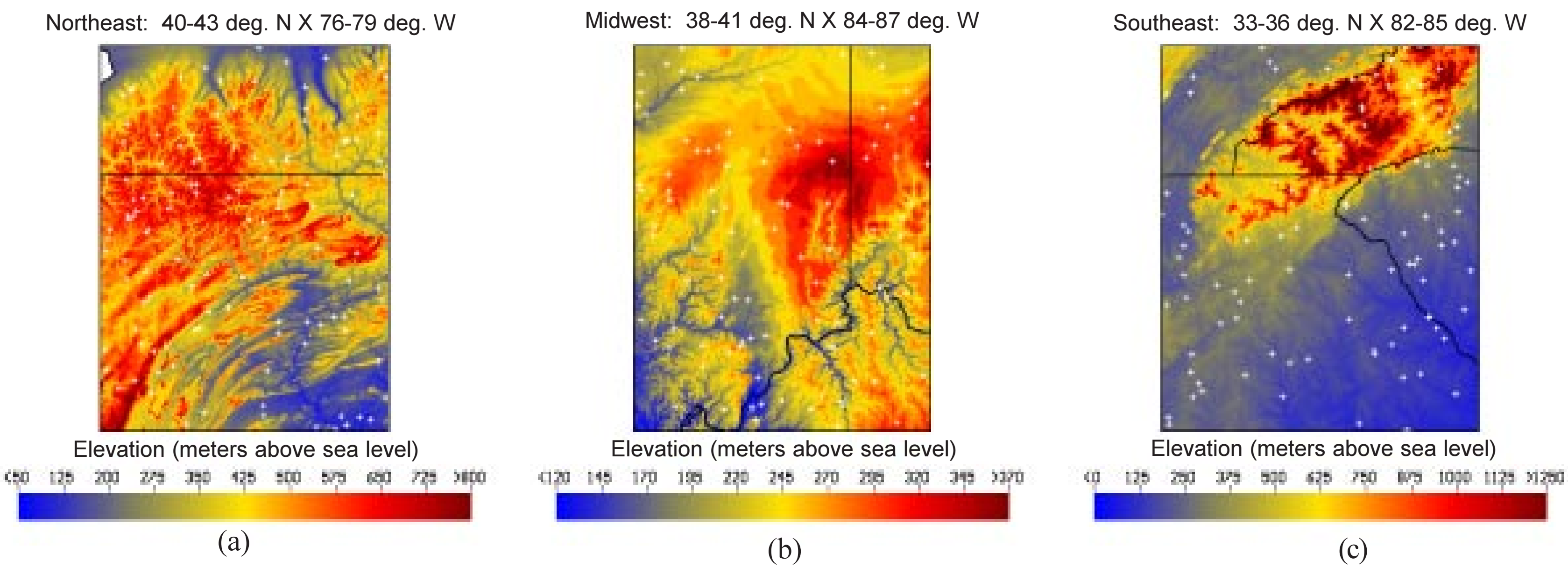


Figure 2. Digital elevation data for three regional plots in the eastern United States. Locations of NOAA cooperative precipitation sites are indicated by a "+".

performance metrics as follows:

$$f_{ryq} = \left(\sum_{I=1}^{n} |o_i - d_i|\right)/k = \quad \text{mean region- and year-specific quarterly error,}$$

$$F_q = \left(\sum_{r=1}^{3} \sum_{y=1}^{3} f_{ryq}\right)/9 = \text{ mean quarter-specific error,}$$

$$F_r = \left(\sum_{y=1}^{3} \sum_{q=1}^{4} f_{ryq}\right)/12 = \quad \text{regional mean quarterly error, and}$$

$$F = \left(\sum_{r=1}^{3} F_r\right)/3 = \quad \text{overall mean quarterly error.}$$

where,
- q = quarter,
- r = region,
- y = year,
- o_i = observed deposition at i^{th} site during quarter, q, and year, y,
- d_i = predicted deposition for i^{th} site during quarter, q, and year, y, and
- k = number of valid performance evaluation sites in region, r, during year, y.

The f_{ryq} were arithmetically averaged over years and regions because the number of valid sites for performance evaluation varied both among years and regions. Simply averaging all evaluation sites for all years and regions would have resulted in unequal emphasis on individual years and regions.

The effect of elevation smoothing on the performance of the WLLSR model was also examined by applying the algorithm with the optimized weighting parameters to DEM data which was locally averaged to radii of 1.61 and 2.41 km (1 and 1.5 miles), as well as to unsmoothed data. Corresponding slope/aspect values were recalculated from each of the smoothed DEM data sets. Elevation smoothing effects were evaluated using the above performance metrics.

Once the optimal weighting function parameters were selected, relative importance (RI) values were calculated for each predictor in the WLLSR model. These RI values are the partial regression sums of squares for the predictors normalized to a sum of one and indicate the proportion of the regression variance attributable to each predictor. The RI values were summarized by averaging over 1990, 1991, and 1992 for each quarter and region. The predictors were further categorized as either coordinate, elevational, or slope/aspect variables and RI values for the categories determined by summing the component predictor RI values.

Although the NADP/NTN yields concentration data for several ions, this paper will only discuss the application of the WLLSR and MQE models to sulfate and nitrate depositions. Precipitation volume is also modeled because it is a major determinant in wet deposition.

Correction of Sulfate Deposition for Maritime Contributions

In coastal regions, such as Maryland, a significant amount of sulfate deposition originates from natural, oceanic processes (Keene et al., 1986; Wadleigh et al., 1993). To accommodate studies that may be concerned with sulfate loading from only anthropogenic sources, such as those being conducted for Maryland and the Chesapeake Bay watershed, sulfate deposition estimates produced by the WLLSR procedures were adjusted by applying a "sea-salt correction" factor. This correction removes the sulfate loading attributable to oceanic aerosol inputs from the estimated total wet sulfate deposition. Wadleigh et al. (1993) indicated that oceanic contributions to sulfate concentrations in precipitation can be estimated by applying a factor of 0.14 to the portion of the chloride in the precipitation that originated from marine sources. By adjusting for the ratio of the molecular weights of sulfate and chloride ions, the factor proposed by Wadleigh et al. (1993) can be applied to estimates of chloride deposition attributable to oceanic inputs to produce estimates of marine-based sulfate deposition as follows:

$$SO_{4m}=0.14*K*Cl_m$$

where, SO_{4m} = sulfate deposition due to marine input,
Cl_m = chloride deposition due to marine input,
K = 2.7095, the ratio of the molecular weight of sulfate (96.0616) to that of chloride (35.453).

The marine contribution to chloride deposition, Cl_m, can be estimated by subtracting an estimate of background terrestrial chloride deposition from the estimate of total chloride deposition. The WLLSR algorithm described above was applied to chloride concentration data from the NADP/NTN to produce estimates of total chloride deposition for the region in and around the Chesapeake Bay watershed, located in portions of Delaware, Maryland, New York, Pennsylvania, and Virginia. Background chloride deposition values for this area were estimated by averaging the total chloride deposition values within a series of three, 1-degree (latitude and longitude) blocks located approximately 500 to 600 km inland from the Atlantic coast and approximately 170 to 250 km to the west of the Chesapeake Bay Watershed. This background sampling region was selected by examining a map of estimated chloride deposition and noting where the pronounced high chloride levels along the coast had dropped to a relatively uniform inland low level. The background sampling region was also selected to be as close to the Chesapeake Bay basin as possible in the direction of the prevailing winds. Background chloride values were sampled at intervals of 0.0033 degrees of latitude and longitude within each of 1-degree block in the background region (i.e., 90,000 samples per block). The mean background chloride deposition estimate was then subtracted from the total chloride deposition estimate for the Chesapeake Bay watershed to produce Cl_m and then SO_{4m}, using the above formula. SO_{4m}, in turn is the "sea-salt" correction for sulfate and was subtracted from estimates of total sulfate deposition to predict anthropogenic sulfate deposition to the Chesapeake Bay watershed.

Precipitation volume and chemistry data from five Pennsylvania, three Maryland, and one northern Virginia sites were used to evaluate and compare the accuracy with which the WLLSR and MQE algorithms estimated wet deposition of sulfate and nitrate within the Chesapeake Bay watershed. These evaluation sites were not part of the NADP/NTN or NOAA monitoring programs.

The five Pennsylvania sites are part of the Pennsylvania Atmospheric Deposition Monitoring Network that is supported by the Pennsylvania Department of Environmental Protection and operated according to NADP/NTN sampling and analytical protocols (Lynch et al., 1999). The Mill Run site in Northern Virginia and the Catoctin Mountain site in Maryland were operated by the United States Geological Survey to provide weekly precipitation chemistry and volume measurements in support of an effects research program. The remaining two sites in Maryland were operated by the Maryland Department of Natural Resources also on a weekly basis. Data from 1984 through 1993 was used from each site, when available, for the model evaluation. Some sites were only in operation for a portion of the 1984-93 period. The weekly observations from each site were aggregated into quarterly wet deposition estimates which were then compared to the estimates from the deposition models.

Results and Discussion

Mean quarterly and annual estimation errors associated with the best identified set of weighting and smoothing function parameters for the WLLSR model are shown in Table 1. Differences in size of absolute errors between estimates of precipitation and sulfate and nitrate depositions are due almost entirely to differences in the magnitude of the estimated phenomena (Table 2) and are reflected by the nearly equal percent estimation errors. Differences among regions in mean quarterly absolute errors for each of the estimated phenomena are also approximately proportional to the mean size of the estimated values. However, the mean quarterly percent errors suggest that, proportionally, precipitation and wet deposition estimates were slightly better for the Midwest region and somewhat poorer for the Southeast region. The mean quarterly percentage errors were greatest in the region of greatest topographic relief and lowest in the region with the most level topography. Surprisingly, this pattern did not hold for the mean annual percent errors with the Northeast being the most poorly estimated region. The annual errors are calculated from the difference of the summed quarterly observations and estimates and, therefore, can incorporate offsetting quarterly estimation errors within each year. Tallying the frequencies of under- and over-estimated quarterly precipitation values reveals that 12.7 and 16.5 percent of the sample sites in the Northeast were either under- or over-estimated for all 4 quarters, respectively. The corresponding unanimous under- and over-estimation rates for the Midwest were 8.3 and 8.9 percent and for the Southeast 3.7 and 8.7 percent. Thus, although precipitation was more poorly estimated in the Southeast on a quarterly basis, a consistent site-specific bias at some of the sites in the Northeast resulted in somewhat poorer annual estimates. Sulfate and nitrate deposition estimates exhibited very similar regional patterns of quarterly under- and over-estimations.

With one exception, the parameters identified as optimal for the distance weighting function in the WLLSR model were very similar for estimation of precipitation and sulfate and nitrate deposition; particularly in regard to d_{max}, the maximum data inclusion radius. The large optimal d_{max} value for estimating precipitation in the Northeast region is in contrast to the much smaller d_{max} values selected for sulfate and nitrate deposition. In general, optimal d_{max} values were highest in the topographically simple Midwest region and were lower in mountainous regions. The range of parameters evaluated for the distance weighting function produced a wider range of estimation

Table 1. WLLSR model weighting and elevation smoothing parameters selected by trial and the corresponding estimation errors (percent errors). Weighting and smoothing functions were adjusted in the sequence listed and the selected overall parameters were used for successive function adjustments. The initial model parameters were v_{max}=278 km, a=1, b=1, u_{max}=4.0, c=0, d=0, n=5, and radius=0.0 km.

Deposition Measurement	Model function adjusted	Region	Best parameter set	Mean quarterly error for best regional parameter set	Mean quarterly error for best overall parameter set	Mean annual error for best overall parameter set
Precipitation (Inches)	Distance weighting	Midwest	v_{max}=222, a=1, b=8	1.615	1.620 (16.3)	3.572 (8.3)
		Northeast	v_{max}=306, a=1,b=6	1.630	1.640 (17.2)	4.439 (11.3)
		Southeast	v_{max}=167, a=1,b=4	2.346	2.356 (21.0)	4.724 (9.2)
		Overall	v_{max}=195, a=1,b=6	1.872	1.872 (18.2)	4.245 (9.6)
	Residual weighting	Midwest	u_{max}=3.0,c=2,d=1	1.607	1.608 (16.1)	3.564 (8.2)
		Northeast	u_{max}=5.5,c=2,d=2	1.637	1.638 (17.3)	4.429 (11.4)
		Southeast	u_{max}=6.0,c=1,d=3	2.346	2.350 (20.6)	4.692 (9.1)
		Overall	u_{max}=4.5,c=2,d=2	1.865	1.865 (18.1)	4.223 (9.5)
	Elevation balancing	Midwest	n=5	1.608	1.608 (16.1)	3.564 (8.2)
		Northeast	n=5	1.638	1.638 (17.3)	4.429 (11.3)
		Southeast	n=1	2.302	2.350 (20.4)	4.692 (8.7)
		Overall	n=5	1.865	1.865 (18.1)	4.223 (9.5)
	Elevation smoothing	Midwest	radius=1.6	1.605	1.605 (16.1)	3.617 (8.3)
		Northeast	radius=1.6	1.635	1.635 (17.3)	4.452 (11.4)
		Southeast	radius=2.4	2.299	2.309 (20.4)	4.755 (9.2)
		Overall	radius=1.6	1.850	1.850 (17.9)	4.247 (9.7)
Sulfate deposition (kg/ha)	Distance weighting	Midwest	v_{max}=195,a=1,b=7	1.047	1.047 (16.4)	2.375 (8.9)
		Northeast	v_{max}=139,a=1,b=5	1.130	1.132 (17.9)	3.151 (12.1)
		Southeast	v_{max}=167,a=1,b=6	0.859	0.869 (21.4)	1.842 (10.1)
		Overall	v_{max}=195,a=1,b=7	1.016	1.016 (18.6)	2.456 (10.4)
	Residual weighting	Midwest	u_{max}=3.0,c=2,d=1	1.033	1.033 (16.0)	2.365 (8.8)
		Northeast	u_{max}=3.0,c=0,d=0	1.126	1.126 (17.8)	3.136 (11.9)
		Southeast	u_{max}=6.0,c=1,d=2	0.865	0.867 (21.0)	1.803 (10.0)
		Overall	u_{max}=3.5,c=2,d=1	1.009	1.009 (18.3)	2.435 (10.2)
	Elevation balancing	Midwest	n=5	1.033	1.033 (16.0)	2.365 (8.8)
		Northeast	n=5	1.126	1.126 (17.7)	3.136 (11.9)
		Southeast	n=1	0.846	0.867 (21.0)	1.803 (9.5)
		Overall	n=5	1.009	1.009 (18.3)	2.435 (10.2)
	Elevation smoothing	Midwest	radius=1.6	1.031	1.031 (16.0)	2.432 (9.0)
		Northeast	radius=1.6	1.125	1.125 (17.7)	3.169 (12.1)
		Southeast	radius=2.4	0.837	0.851 (20.6)	1.806 (9.9)
		Overall	radius=1.6	1.002	1.002 (18.1)	2.469 (10.3)
Nitrate Deposition (kg/ha)	Distance weighting	Midwest	v_{max}=222,a=1,b=8	0.581	0.582 (16.4)	1.316 (8.9)
		Northeast	v_{max}=139,a=1,b=5	0.752	0.752 (18.0)	2.070 (11.9)
		Southeast	v_{max}=167,a=1,b=6	0.460	0.465 (21.3)	0.981 (9.8)
		Overall	v_{max}=195,a=1,b=7	0.600	0.600 (18.6)	1.456 (10.3)
	Residual weighting	Midwest	u_{max}=3.5,c=2,d=2	0.574	0.575 (16.0)	1.314 (8.8)
		Northeast	u_{max}=4.5,c=2,d=1	0.751	0.572 (17.9)	2.075 (11.8)
		Southeast	u_{max}=6.0,c=1,d=2	0.463	0.465 (21.0)	0.974 (9.9)
		Overall	u_{max}=4.0,c=2,d=2	0.597	0.597 (18.3)	1.454 (10.2)
	Elevation balancing	Midwest	n=5	0.575	0.575 (16.0)	1.314 (8.8)
		Northeast	n=6	0.751	0.752 (17.8)	2.075 (11.8)
		Southeast	n=1	0.452	0.465 (20.9)	0.974 (9.5)
		Overall	n=5	0.597	0.597 (18.3)	1.454 (10.2)
	Elevation smoothing	Midwest	radius=1.6	0.573	0.573 (16.0)	1.346 (9.0)
		Northeast	radius=1.6	0.749	0.749 (17.8)	2.089 (11.9)
		Southeast	radius=2.4	0.447	0.454 (20.6)	0.951 (9.6)
		Overall	radius=1.6	0.592	0.592 (18.1)	1.462 (10.2)

Table 2. Mean annual precipitation and interpolated (MQE) sulfate and nitrate deposition at NOAA sites within each region.

Region	Precipitation (Inches)	Sulfate Deposition (kg/ha)	Nitrate Deposition (kg/ha)
Midwest	43.8	27.6	15.4
Northeast	40.3	27.2	18.0
Southeast	53.9	18.9	10.2
Overall	46.0	24.6	14.5

errors than other weighting and smoothing functions. Overall quarterly percent errors for precipitation, and sulfate and nitrate deposition estimates ranged from 18.2 to 19.8, 18.6 to 22.2, and 18.6 to 22.3 percent, respectively, for the array of parameters tested.

The selected parameters for the residual weighting function were most consistent in the Southeast region, where s_{max}, the maximum absolute studentized residual, was higher than for the other two regions. Values of s_{max} for the Northeast region varied markedly for the three estimated deposition phenomena. The highest s_{max} value for the Northeast was observed for precipitation estimation and coincided with the unusually large d_{max} value in the distance weighting function. Residual weighting improved estimate accuracy in all regions except for nitrate deposition estimation in the Northeast region. Overall, quarterly percent errors for precipitation and sulfate and nitrate depositions ranged from 18.1 to 18.3, 18.3 to 18.5, and 18.3 to 18.7 percent, respectively, for the array of parameters examined.

The optimal number of elevation intervals, N_e, used for elevation balancing was quite consistent within each region for all estimates. For the Midwest and Northeast regions either 5 or 6 intervals yielded the best estimates. In contrast, elevation balancing was never beneficial in the Southeast region. Overall, quarterly percent errors for precipitation ranged from 18.1 to 18.2 percent and for both sulfate and nitrate deposition they ranged from 18.3 to 18.6 percent. The poorest estimates generally occurred when 2 or 3 elevation intervals were used.

Smoothing the elevation data used in the WLLSR model improved estimate accuracy in all regions. Smoothing the DEM data to a radius of 1.6 km (1 mile) produced the best estimates in the Midwest and Northeast regions. A smoothing radius of 2.4 km (1.5 miles) consistently yielded the lowest errors in the Southeast region. Overall, quarterly percent errors for precipitation and sulfate and nitrate depositions ranged from 17.9 to 18.1, 18.1 to 18.3, and 18.1 to 18.4 percent, respectively, for the smoothing radii evaluated. The role of elevation smoothing in improving model performance is likely related to the uncertainty in the location of the NOAA precipitation stations. The coordinates for these stations are only available to the nearest minute of a degree and, therefore, may result in a location error of approximately 1.3 km. A location error of this size could dramatically affect the indicated topographic situation of a station in mountainous terrain. Elevation smoothing de-emphasizes the localized features in the DEM data and, thus, moderates possible errors in topographic positioning.

For all wet deposition estimates and for all quarters the WLLSR model produced the poorest fit of the sample data for the Northeast region as evidenced by the mean r^2 values in Tables 3-5. Overall, the WLLSR model fit the sample data for the Southeast region markedly better than for the Midwest region. With only two exceptions, the fit of both the sulfate and nitrate deposition data exceeded that of the precipitation observations in all regions for all quarters. The poor fit of precipitation data relative to the deposition data is probably, in part, a result of the uncertainty in the location of the NOAA precipitation stations. Because precipitation volume is influenced by orographic factors, inaccurate location of precipitation stations relative to the local terrain can be expected to negatively impact estimate quality. In contrast, the deposition data, while containing a precipitation component, also incorporates an ion concentration component that is not known to be

Table 3. Model r^2 and predictor relative importance (RI) values for the application of the WLLSR model to precipitation data. RI and r^2 values are averaged over 1990, 1991, and 1992 for each region and quarter.

	Midwest					Northeast					Southeast				
Parameter	Qtr. Mean	Dec-Feb	Mar-May	Jun-Aug	Sep-Nov	Qtr. Mean	Dec-Feb	Mar-May	Jun-Aug	Sep-Nov	Qtr. Mean	Dec-Feb	Mar-May	Jun-Aug	Sep-Nov
Model r^2	0.412	0.591	0.371	0.317	0.370	0.239	0.263	0.251	0.234	0.210	0.452	0.574	0.483	0.356	0.395
x	0.083	0.108	0.064	0.078	0.083	0.060	0.030	0.080	0.064	0.065	0.038	0.035	0.056	0.024	0.037
y	0.056	0.049	0.068	0.050	0.059	0.060	0.054	0.048	0.081	0.058	0.058	0.065	0.067	0.050	0.051
xy	0.041	0.035	0.048	0.053	0.029	0.043	0.040	0.049	0.039	0.042	0.043	0.038	0.044	0.047	0.044
x2	0.114	0.148	0.105	0.070	0.132	0.072	0.061	0.092	0.058	0.077	0.038	0.033	0.051	0.031	0.036
y2	0.218	0.220	0.241	0.161	0.250	0.115	0.121	0.050	0.199	0.092	0.086	0.091	0.109	0.057	0.087
Coordinate Sum	0.513	0.560	0.527	0.412	0.553	0.350	0.306	0.319	0.441	0.334	0.263	0.261	0.327	0.209	0.255
e	0.059	0.036	0.071	0.077	0.051	0.082	0.098	0.096	0.073	0.062	0.111	0.109	0.145	0.069	0.123
ex	0.049	0.036	0.058	0.054	0.047	0.062	0.086	0.068	0.044	0.050	0.083	0.090	0.117	0.045	0.082
ey	0.058	0.037	0.074	0.074	0.048	0.072	0.088	0.088	0.062	0.051	0.096	0.088	0.103	0.070	0.124
Elevation Sum	0.166	0.109	0.202	0.205	0.146	0.217	0.271	0.253	0.179	0.163	0.291	0.287	0.364	0.183	0.329
East	0.091	0.072	0.073	0.120	0.100	0.098	0.071	0.051	0.140	0.129	0.163	0.170	0.106	0.195	0.179
West	0.082	0.114	0.060	0.089	0.063	0.115	0.113	0.095	0.113	0.141	0.096	0.102	0.070	0.158	0.057
North	0.074	0.077	0.077	0.089	0.054	0.103	0.083	0.121	0.080	0.130	0.121	0.101	0.075	0.193	0.116
South	0.075	0.068	0.060	0.086	0.084	0.117	0.156	0.161	0.048	0.103	0.066	0.078	0.058	0.063	0.064
Slope/Aspect Sum	0.322	0.331	0.271	0.384	0.301	0.434	0.423	0.428	0.381	0.503	0.446	0.452	0.309	0.608	0.416

Table 4. Model r^2 and predictor relative importance (RI) values for the application of the WLLSR model to sulfate deposition data. RI and r^2 values are averaged over 1990, 1991, and 1992 for each region and quarter.

	Midwest					Northeast					Southeast				
Parameter	Qtr. Mean	Dec-Feb	Mar-May	Jun-Aug	Sep-Nov	Qtr. Mean	Dec-Feb	Mar-May	Jun-Aug	Sep-Nov	Qtr. Mean	Dec-Feb	Mar-May	Jun-Aug	Sep-Nov
Model r^2	0.431	0.451	0.428	0.428	0.418	0.334	0.386	0.318	0.284	0.347	0.559	0.691	0.637	0.394	0.515
x	0.099	0.113	0.111	0.074	0.098	0.078	0.076	0.089	0.076	0.071	0.126	0.128	0.155	0.085	0.137
y	0.057	0.061	0.062	0.051	0.055	0.069	0.053	0.048	0.091	0.083	0.053	0.063	0.050	0.047	0.054
xy	0.042	0.048	0.038	0.052	0.031	0.043	0.042	0.052	0.043	0.034	0.050	0.040	0.057	0.035	0.070
x2	0.139	0.161	0.178	0.065	0.153	0.129	0.148	0.128	0.118	0.122	0.127	0.117	0.137	0.112	0.141
y2	0.207	0.154	0.262	0.228	0.184	0.136	0.112	0.065	0.210	0.156	0.074	0.093	0.070	0.062	0.071
Coordinate Sum	0.545	0.537	0.650	0.471	0.521	0.454	0.431	0.382	0.537	0.465	0.431	0.442	0.469	0.340	0.473
e	0.066	0.046	0.066	0.074	0.077	0.080	0.100	0.084	0.075	0.062	0.090	0.084	0.121	0.072	0.085
ex	0.055	0.046	0.054	0.051	0.070	0.061	0.088	0.060	0.045	0.049	0.068	0.069	0.097	0.047	0.057
ey	0.065	0.047	0.069	0.071	0.072	0.071	0.090	0.078	0.064	0.051	0.078	0.068	0.086	0.073	0.085
Elevation Sum	0.185	0.139	0.188	0.196	0.219	0.212	0.278	0.222	0.184	0.162	0.236	0.221	0.304	0.191	0.227
East	0.071	0.064	0.039	0.102	0.079	0.069	0.051	0.051	0.081	0.091	0.115	0.126	0.050	0.156	0.127
West	0.068	0.100	0.040	0.073	0.061	0.082	0.061	0.071	0.093	0.103	0.077	0.077	0.077	0.105	0.048
North	0.066	0.091	0.050	0.079	0.043	0.072	0.057	0.096	0.058	0.080	0.094	0.072	0.068	0.161	0.077
South	0.065	0.069	0.034	0.079	0.076	0.111	0.121	0.178	0.047	0.098	0.047	0.062	0.031	0.047	0.048
Slope/Aspect Sum	0.270	0.324	0.163	0.334	0.259	0.334	0.291	0.396	0.279	0.372	0.333	0.337	0.227	0.469	0.300

Table 5. Model r^2 and predictor relative importance (RI) values for the application of the WLLSR model to nitrate deposition data. RI and r^2 values are averaged over 1990, 1991, and 1992 for each region and quarter.

	Midwest					Northeast					Southeast				
Parameter	Qtr. Mean	Dec-Feb	Mar-May	Jun-Aug	Sep-Nov	Qtr. Mean	Dec-Feb	Mar-May	Jun-Aug	Sep-Nov	Qtr. Mean	Dec-Feb	Mar-May	Jun-Aug	Sep-Nov
Model r^2	0.417	0.418	0.399	0.430	0.421	0.343	0.377	0.309	0.285	0.400	0.525	0.634	0.654	0.345	0.465
x	0.092	0.079	0.121	0.088	0.080	0.078	0.059	0.096	0.073	0.086	0.103	0.089	0.147	0.054	0.121
y	0.054	0.047	0.062	0.054	0.052	0.070	0.061	0.065	0.085	0.069	0.056	0.062	0.046	0.056	0.061
xy	0.048	0.054	0.045	0.058	0.034	0.045	0.057	0.053	0.037	0.032	0.049	0.036	0.048	0.045	0.067
x2	0.123	0.138	0.169	0.066	0.121	0.121	0.109	0.128	0.105	0.141	0.100	0.087	0.132	0.068	0.112
y2	0.190	0.150	0.240	0.206	0.163	0.127	0.093	0.065	0.229	0.122	0.071	0.109	0.056	0.054	0.066
Coordinate Sum	0.507	0.467	0.637	0.473	0.450	0.441	0.379	0.407	0.529	0.450	0.379	0.383	0.430	0.277	0.428
e	0.070	0.059	0.070	0.072	0.078	0.082	0.104	0.086	0.068	0.070	0.094	0.078	0.132	0.086	0.079
ex	0.059	0.059	0.057	0.050	0.071	0.063	0.092	0.061	0.042	0.056	0.072	0.067	0.110	0.059	0.055
ey	0.069	0.060	0.073	0.069	0.072	0.072	0.094	0.079	0.058	0.057	0.078	0.062	0.090	0.085	0.077
Elevation Sum	0.198	0.178	0.200	0.191	0.221	0.217	0.290	0.225	0.168	0.184	0.245	0.207	0.332	0.230	0.210
East	0.085	0.073	0.043	0.108	0.116	0.070	0.057	0.049	0.085	0.090	0.133	0.162	0.050	0.156	0.165
West	0.073	0.113	0.044	0.071	0.065	0.087	0.066	0.078	0.101	0.103	0.085	0.088	0.085	0.117	0.051
North	0.067	0.096	0.046	0.072	0.055	0.077	0.075	0.087	0.071	0.075	0.106	0.087	0.073	0.171	0.093
South	0.071	0.074	0.030	0.085	0.093	0.108	0.133	0.154	0.047	0.098	0.052	0.073	0.030	0.050	0.054
Slope/Aspect Sum	0.296	0.355	0.163	0.336	0.329	0.342	0.331	0.368	0.304	0.367	0.376	0.410	0.238	0.493	0.362

as strongly elevational dependent as precipitation. Thus, the spatial inaccuracies inherent to the NOAA data would have less of an impact on the models ability to account for the concentration component of deposition. A consistent seasonal pattern in the degree of model fit was apparent in all regions for both precipitation and sulfate deposition data. For these deposition measurements, model fit tended to be best in the December-February quarter when snowfall made its greatest contribution to precipitation volume. Model fit was poorer in the warmer quarters and generally

poorest during the June-August quarter when isolated convective thunderstorm activity is most prevalent. Fit of the WLLSR model to nitrate deposition data in the Southeast region also exhibited this same seasonal pattern. Degree of model fit for nitrate deposition in the Northeast region also reached a low during the June-August quarter, but peaked during September to November. In contrast, model fit for nitrate deposition data in the Midwest was greatest during the summer quarter.

The contribution of individual predictors to the fit of the WLLSR model also exhibited regional and seasonal patterns. The regressions sums of squares of the predictors, standardized to a sum of 1.0, represent the relative importance of each predictor to model fit (see Tables 3-5). Grouping the predictors into three functional categories and summing the relative importance values for each category simplifies interpretation of the regional and seasonal patterns in contribution to model fit. In the Midwest region, the contribution of the coordinate group of predictors, which express the location of observations only in the latitudinal and longitudinal dimensions, was markedly more important than that of the elevation or slope/aspect predictor groups for all deposition measurements. Accordingly, the relative importance of the elevation and slope/aspect groups to model fit for the Midwest was generally lower than that in the Northeast and Southeast regions. The observed relative contribution of predictor groups in the Midwest is as expected considering that the terrain there is relatively level and unlikely to impose strong orographic effects on precipitation. In general, the relative importance of the elevation group of predictors was somewhat greater in the Southeast region than the Northeast region. Further, the overall contribution of the slope/aspect group to model fit for the Southeast region was equal to or slightly greater than in the Northeast region. The more extreme range of elevations occurring in the Southeast region likely accounts for the greater importance of elevation and slope/aspect information relative to the Northeast region.

For the northeast region, the relative importance of the coordinate group of predictors was highest during the June-August quarter and was generally lowest during the December-February quarter. In contrast, the contribution of the coordinate group for the Southeast region was weakest during the June-August quarter and peaked in either the March-May or September-November quarters. The elevation group of predictors were most influential on model fit for the Northeast region during the December-February quarter and least important in the summer and fall quarters. In the Southeast region, the elevation group's contribution was greatest in the March-May quarter and was low to moderate during the winter quarter. The seasonal patterns in the relative importance of the predictor groups for the Midwest region show little consistency among the three deposition measurements. The observed differences in the seasonal patterns of predictor group importance among regions is likely due to differing amounts of snowfall received by each region and the effects of topography on snowfall distribution. In the mountainous Northeast region, precipitation during

Table 6. A comparison of mean quarterly and mean annual estimation errors (percent errors) for the MQE and optimized WLLSR deposition models.

		Mean quarterly estimation errors		Mean annual estimation errors		Percent reduction produced by WLLSR model relative to MQE model	
Deposition Measurement	Region	WLLSR	MQE	WLLSR	MQE	Mean quarterly est. errors	Mean annual est. errors
Precipitation (Inches)	Midwest	1.60 (16.1)	1.69 (16.7)	3.62 (8.3)	3.97 (9.1)	5.1	8.9
	Northeast	1.64 (17.3)	2.02 (21.3)	4.45 (11.4)	5.92 (15.1)	19.3	24.8
	Southeast	2.31 (20.4)	2.88 (24.7)	4.76 (9.2)	6.21 (11.5)	19.9	23.5
	Overall	1.85 (17.9)	2.20 (20.9)	4.25 (9.7)	5.37 (11.9)	15.9	20.9
Sulfate Deposition (kg/ha)	Midwest	1.03 (16.0)	1.09 (16.7)	2.43 (9.0)	2.66 (9.8)	5.4	8.5
	Northeast	1.12 (17.7)	1.37 (21.3)	3.17 (12.1)	4.16 (15.9)	18.1	23.7
	Southeast	0.85 (20.6)	1.01 (24.8)	1.81 (9.9)	2.18 (11.8)	15.9	17.3
	Overall	1.00 (18.1)	1.16 (20.9)	2.47 (10.3)	3.00 (12.5)	13.5	17.7
Nitrate Deposition (kg/ha)	Midwest	0.57 (16.0)	0.61 (16.7)	1.35 (9.0)	1.45 (9.6)	5.6	7.3
	Northeast	0.75 (17.8)	0.90 (21.3)	2.09 (11.9)	2.71 (15.5)	17.1	23.0
	Southeast	0.45 (20.6)	0.54 (24.7)	0.95 (9.6)	1.18 (11.8)	15.9	19.5
	Overall	0.59 (18.1)	0.68 (20.9)	1.46 (10.2)	1.78 (12.3)	13.5	18.0

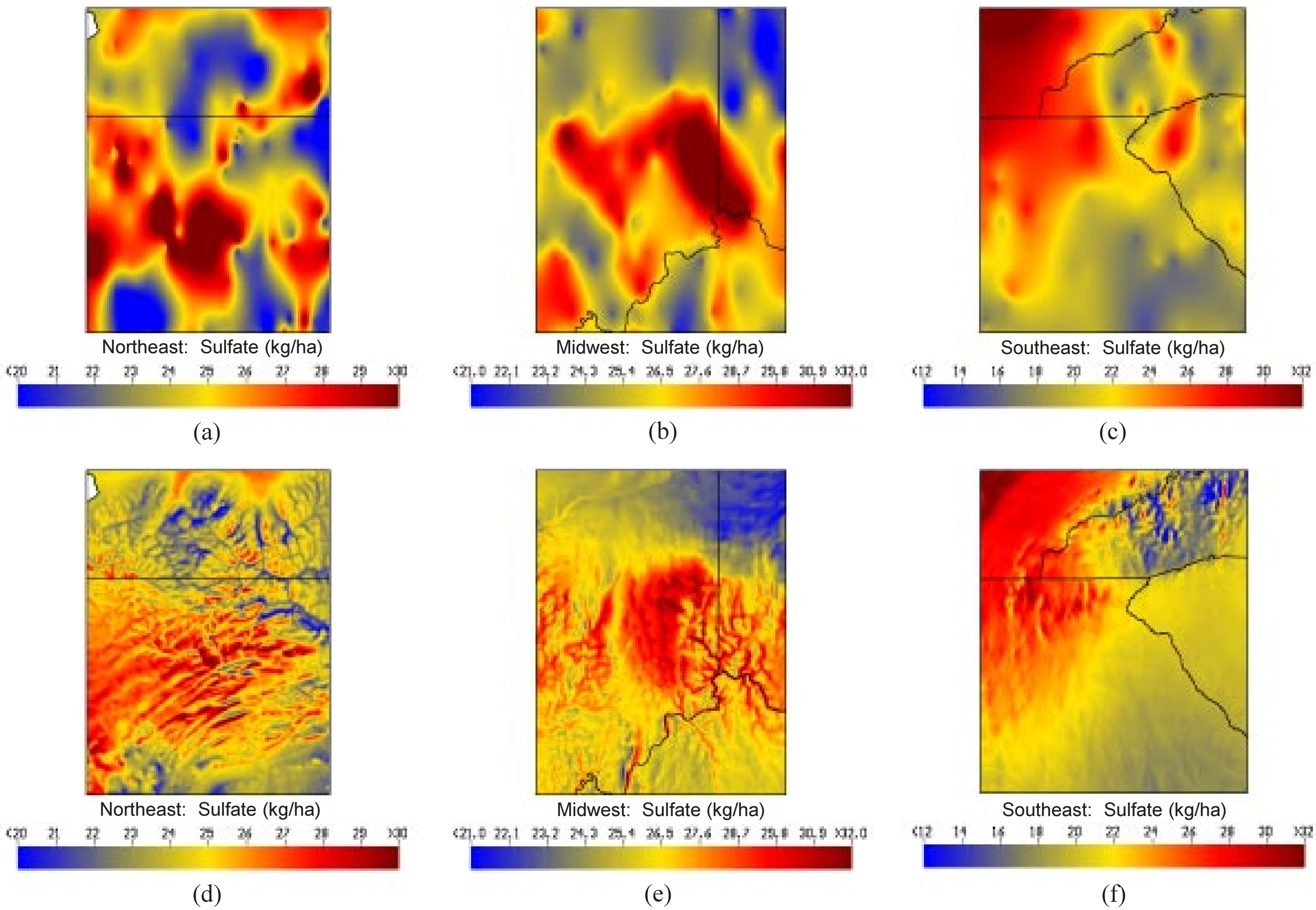


Figure 3. Estimated 1991 annual wet sulfate deposition in three regional plots in the eastern United States. Estimates in maps a-c (upper row) and d-f (lower row) were produced using the MQE and WLLSR algorithms, respectively.

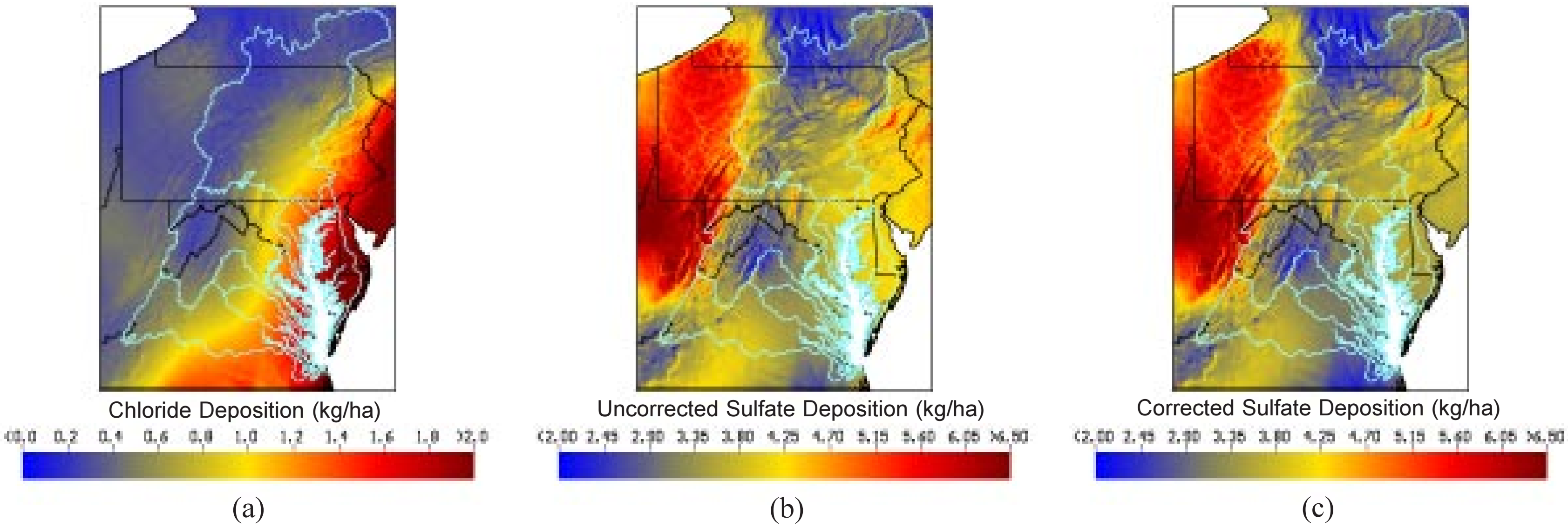


Figure 4. Chloride and uncorrected and "seasalt"-corrected sulfate deposition estimates for the Chesapeake Bay drainage area (green) during the winter quarter of 1990-91 (December through February). Maps a and b show direct estimates from the WLLSR model. The sulfate deposition estimates in c reflect the removal of sulfate from marine orgins, as predicted from the chloride deposition estimates in a.

the winter quarter is predominantly snowfall which is generally heaviest at higher elevations. The Midwest region, also generally receives a large proportion of its winter precipitation as snow but lacks the topographic relief to strongly influence snowfall distribution. Although a large portion of the Southeast region is mountainous, the distribution of snowfall is much more limited than in the other regions.

The WLLSR model yielded better estimates for all deposition measurements in all regions than did the two-dimensional MQE algorithm (see Table 6 and Figure 3). The greatest improvements in estimate accuracy occurred in the two mountainous regions. The improvement of estimates for the relatively level Midwest region were only about 30 percent of those observed in the Northeast and Southeast regions. Not surprisingly, the topographically enhanced WLLSR model

offers greater improvements in estimation accuracy in areas having greater topographic relief. Annual estimation errors were consistently improved more by the WLLSR model than were mean quarterly estimation errors.

The improvements in estimate accuracy relative to the two-dimensional algorithm were generally somewhat greater for precipitation than for sulfate and nitrate depositions. As noted earlier, sulfate and nitrate deposition observations contain a concentration component which is distributed in only two dimensions without regard to elevation. The MQE algorithm is well suited for modeling this concentration component of deposition and, consequently, the WLLSR model would not be expected to have as great of a performance advantage as for precipitation estimation.

The application of the “sea-salt” correction to sulfate deposition estimates for the Chesapeake Bay watershed during the Winter of 1990-91 is illustrated in Figure 4. The prevalence of storms following a coastal track is generally greatest during Winter and Spring seasons along the Mid-Atlantic and Northeast coastal regions of the United States. Accordingly, the marine influence on precipitation chemistry is strongest during those seasons. The zone of marine influence is readily apparent in the coastal states on the chloride deposition map (Figure 4a). Removal of the estimated marine-contributed sulfate deposition produced subtle, but noticeable, changes in the sulfate deposition estimates near the coastline (Figures 4a and 4b). The “sea-salt” adjustment to sulfate deposition for southern New Jersey was approximately 0.8 kg/ha during the Winter 1991 quarter, and was approximately 1.7 kg/ha for all of 1991.

The results of the comparing sulfate and nitrate wet deposition estimates from the WLLSR and MQE algorithms to the observations from the nine evaluation sites in the Chesapeake Bay watershed are summarized in Table 7 as mean annual errors. Overall, the WLLSR model improved on the estimation errors of the 2-dimensional MQE algorithm by about 22 percent for sulfate deposition and 19 percent for nitrate deposition. The greatest improvements in estimate accuracy occurred at the Elliott and Hills Creek State Park sites in Pennsylvania and the Mill Run site in Virginia. These three sites are located in relatively mountainous terrain compared to most of the other sites. In contrast to the overall pattern, the WLLSR estimates were generally poorer than the

Table 7. A comparison of estimation errors between the multi-quadric equations (MQE) and weighted linear least square (WLSR) deposition estimation algorithms. Wet sulfate and nitrate deposition observations from 9 non-NADP/NTN precipitation chemistry monitoring sites within the Chesapeake Bay Watershed were used for the comparison. The available data for each site from 1984 through 1993 were incorporated in the analyses.

				Wet Sulfate Deposition				Wet Nitrate Deposition			
				Mean annual absolute estimation error (kg/ha) (observed-predicted)		Mean annual percent estimation error 100x(obs.-est.)/obs.		Mean annual absolute estimation error (kg/ha) (observed-predicted)		Mean annual percent estimation error 100x(obs.-est.)/obs.	
Site	Latitude (DMS)	Longitude (DMS)	Data from years	MQE	WLSR	MQE	WLSR	MQE	WLSR	MQE	WLSR
Pennsylvania:											
Elliott S. P.	41 7 2	78 31 40	1989-93	7.15	4.86	19.5	13.3	2.95	1.43	13.6	6.6
Gettysburg N. P.	39 49 31	77 17 16	1984-93	2.64	3.52	8.2	10.5	2.71	3.44	12.8	15.4
Hills Creek S. P.	41 48 24	77 11 29	1984-93	5.15	2.35	20.6	9.4	2.83	1.86	17.5	11.0
Little Buffalo S. P.	40 27 26	77 10 3	1984-93	2.84	2.52	9.6	8.2	1.92	2.39	8.4	10.3
Little Pine S. P.	41 21 50	77 21 32	1984-93	3.96	4.19	12.7	13.1	2.18	2.32	9.8	10.5
Maryland:											
Catoctin Mt.	39 37 36	77 28 51	1984-91	3.52	4.22	12.9	14.3	3.16	2.24	21.4	15.3
Elms	38 12 6	76 22 31	1985-92	3.17	2.57	14.5	11.5	2.11	1.70	15.7	12.5
Rocky Gap S. P.	39 43 12	78 38 3	1985-93	3.71	2.22	15.1	8.7	2.05	1.51	13.0	9.4
Virginia:											
Mill Run	38 52 16	78 21 34	1984-89	5.57	3.02	24.7	13.2	3.20	1.92	22.6	12.8
Mean of Sites				4.19	3.27	15.3	11.4	2.57	2.09	15.0	11.5

MQE predictions at the Gettysburg and Little Pine sites in Pennsylvania. The Gettysburg site is located in the least mountainous terrain of the Pennsylvania sites and may have benefitted less from the elevational component of the WLLSR model. Also, sulfate concentrations at Gettysburg were generally higher than those of the nearest NADP/NTN sites and, thus, may not have been well-represented by the NADP/NTN concentration data on which both estimation algorithms were based. Sulfate was also poorly estimated by the WLLSR model at the Catoctin Mountain site in northern Maryland, in a county directly south of and adjacent to the Gettysburg site. A common localized source of sulfur dioxide emissions could conceivably have influenced both the Gettysburg and Catoctin sites without being represented in the relatively sparse NADP/NTN monitoring network. Another negative factor on the performance of the WLLSR model at the Catoctin site may have been erroneous station coordinates. Precise coordinates were not available for the site and the site description was inadequate to pin-point the station location on a topographic map. As indicated earlier, the WLLSR model is very sensitive to errors in site coordinates because they are critical in determining local topographic characteristics, such as elevation and slope/aspect.

The accuracy with which wet sulfate and nitrate depositions at the Chesapeake Bay watershed evaluation sites were estimated agrees very closely with the estimation errors reported earlier for the Northeast study area. Annual sulfate deposition was estimated only slightly less accurately for the Chesapeake Bay watershed than the Northeast study area for both estimation algorithms (3.27 vs. 3.17 kg/ha mean errors for WLLSR and 4.19 vs. 4.16 kg/ha mean errors for MQE). Annual estimates of nitrate deposition were equally as accurate for the WLLSR model for both the Chesapeake Bay watershed and Northeast study area assessments (2.09 kg/ha mean error). Nitrate deposition was somewhat better estimated for the Chesapeake Bay watershed than the Northeast study area by the MQE algorithm (2.57 vs 2.71 kg/ha mean errors).

Conclusions

Overall, mean quarterly and annual deposition estimation errors of 17 and 10 percent, respectively, for the WLLSR model are still rather large; but represent a measurable improvement of those obtained from a two-dimensional algorithm. The improvements obtained by the incorporation of topographic information into modeling of precipitation and wet deposition in this study were probably most limited by the lack of precise coordinates for NOAA stations. Unfortunately, the NOAA cooperative precipitation network represents the only array of precipitation measurement stations covering the eastern U.S. that is of sufficient density to support modeling of local topographic influences on wet atmospheric deposition. With only approximately 220 active sites for the entire U.S., the NADP/NTN network provides a rather sparse distribution of precipitation chemistry monitoring stations. Obviously, a denser precipitation chemistry network would enhance any wet deposition modeling effort. However, the density of the precipitation chemistry network was not a significant factor in the performance assessment in the present study because validation deposition observations were produced by interpolating the available concentration data to the individual NOAA station coordinates.

Future efforts in refining the wet deposition WLLSR model will focus on enhancing estimates of precipitation chemistry concentrations and on refinements that will improve model performance over large bodies of water, such as the Chesapeake Bay. Improvements in precipitation chemistry estimates will center on precipitation volume/concentration relationships as well as the effects of elevation on precipitation chemistry and the scavenging of pollution by precipitation at higher elevations. A dry deposition component will also be incorporated into the model. Potential applications of model output include cause-effect relationships between atmospheric deposition and sensitive aquatic and terrestrial ecosystems, particularly at high elevations; forest health and nitrogen saturation issues; nutrient enrichment of estuaries systems, such as the Chesapeake Bay; critical loads estimates; and the assessment of source/receptor relationships between emissions and wet deposition.

Acknowledgment: Funding for this project was provided by the Maryland Department of Natural Resources under contract CB95-003-004 and by the U.S. Forest Service, Northeast Forest Experiment Station (Cooperative Agreement #23-721) through their Northern Global Climate Change Research Program.

References

Alpert, P. and H. Shafir. 1989. A physical model to complement rainfall normals over complex terrain. *J. Hydrol.*, **110**:51-62.

Barrie, R.G. 1981. *Mountain Weather and Climate*. Methuen, New York, NY USA.

Barros, A.P. and D.P. Lettenmaier. 1994. Dynamic modeling of orographically induced precipitation. *Reviews of Geophysics*, **32**(3):265-284.

Barros, A.P. and D.P. Lettenmaier. 1993. Dynamic modeling of the spatial distribution of precipitation in remote mountainous areas. *Mon. Weather Rev.*, **121**:1195-1214.

Bell, R.S. 1978. The forecasting of orographically enhanced rainfall accumulations using 10-level model data. *Meteorol. Mag.*, **107**:113-124.

Beven, K.J. and M.J. Kirkby. 1978. A physically based variable contributing area model of basin hydrology. *Hydrological Sciences Bulletin*, **24**(1):43-69.

Chaumerliac, R.E. and J.F. Mahouf. 1987. Numerical simulations of orographic enhancement of rain with a mesoscale model. *J. Clim. Appl. Met.*, **26**:661-670.

Colton, D.E. 1976. Numerical simulation of the orographically induced precipitation distribution for use in hydrologic analysis. *J. Clim. Appl. Meteorol.*, **15**:1241-1251.

Dore, A.T., T.W. Choularton, and D. Flowler. 1992. An improved wet deposition map of the United Kingdom incorporating the seeder-feeder effect over mountainous terrain. *Atmos. Environ.* **26A**(8):1375-1381.

Fan, Y. and C.J. Duffy. 1993. Statistical analysis of monthly temperature and precipitation fields on the Wasatch Front. *Water Resources Res.*, **29**(12):4157-4166.

France, L. 1994. Surface land daily cooperative summary of the day. TD-3200. National Climatic Data Center. Asheville, NC.

Grimm, J.W. and J.A. Lynch. 1991. Statistical analysis of errors in estimating wet deposition using five surface estimation algorithms. *Atmos. Environ*., **25A**(2):317-327.

Grimm, J.W. and J.A. Lynch. 1997. *Enhanced Wet Deposition Estimates Using Modeled Precipitation Inputs*. Final Report, USDA, Forest Service, NEFES under Cooperative Agreement 23-721. Penn State University, ERRI. 32 pp.

Hardy, R.L. 1971. Multiquadic equations of topography and other irregular surfaces. *J. Geophysical Res*., **76**:1905-1915.

Hornberger, G.M., K.J. Beven, B.J. Cosby, and D.E. Sappington. 1985. Shenandoah watershed study: Calibration of a topography-based, variable contributing area hydrological model to a small forested catchment. *Water Resources Res.*, **21**(12):1841-1850.

Jones, A. and T.W. Choularton. 1988. A model of wet deposition to complex terrain. *Atmos. Environ.*, **22**(11):2419-2430.

Keene, W.C., A.A.P. Pszenny, J.N. Galloway, and M.E. Hawley. 1986. Sea-salt corrections and interpretation of constituent ratios in marine precipitation. *J. Geophys. Res*., 91:6647-6658.

Lovett, G.M. and J.D. Kinsman. 1990. Atmospheric pollution deposition to high elevation ecosystems. *Atmos. Environ*., **24**:2767-2786.

Lynch, J.A., Horner, K.S., Grimm, J.W. 1999. *Atmospheric deposition: Spatial and Temporal Variations in Pennsylvania, 1998.* Annual technical report to the PA Dept. of Environ. Protection, The Pennsylvania State University, ERRI, ER9905, University Park, PA 210 pp.

Moore, I.D., E.M. O'Loughlin, and G.J. Burch. 1988. A contour-based topographic model for hydrological and ecological applications. *Earth Surface Processes and Landforms*, **13**:305-320.

NADP. 1999. National Atmospheric Deposition Program, Annual Data Summary: Precipitation Chemistry in the United States. NADP Program Office, Illinois State Water Survey, University of Illinois, Champaign, IL USA.

Neilson, R.P. 1992. *A Model for Predicting Continental-Scale Vegetation Distribution and Water Balance*. U.S. EPA, Environ. Res. Lab. Corvallis, OR. 96 pp.

Neter, J. And W. Wasserman. 1974. *Applied Linear Statistical Models*. R.D. Irwin, Inc. Homewood, IL. 842 pp.

NOAA, 1999. National Oceanic and Atmospheric Administration, Air Resources Lab. Atmospheric Integrated Monitoring Network, (AIRMoN)-Dry. http://www.arl.noaa.gov/research/programs.

Ollinger, S.V., G.M. Lovett, S.E. Millham, R.G. Lathrop, and J. M. Ellis. 1993. A spatial model of atmospheric deposition for the northeastern United States. *Ecol. Appl*., **3**:459-472.

Summers, P.W., V.C. Bowersox, and G.L. Stensland. 1986. The geographical distribution and temporal variation of acidic deposition in eastern North America. *Water, Air and Soil Pollution*. **31**:523-535.

Sumner, G. 1988. *Precipitation Process and Analysis*, 455 pp. John Wiley, New York, NY.

U.S. EPA. 1999. Clean Air Status and Trends Network (CASNet) 1998 Annual Report. EPA, Office of Air and Radiation, Acid Rain Division, Washington, DC. http://www.epa/ard/publc/acid rain/old_castnet/index/html.

Wadleigh, M.A., H.P. Schwarcz, and J.R. Kramer. 1993. Sulfur isotope tests of sea salt correction factors in precipitation: Nova Scotia, Canada. *Water, Air and Soil Pollution*. 77:1-16.

Wisniewski, J. and J.D. Kinsman. 1988. pH and hydrogen ion deposition patterns for continental United States and Canada. *Water, Air and Soil Pollution*. **38**:1-17.

Zemba, S.G., D. Golomb, and J.A. Fay. 1988. Wet sulfate and nitrate deposition patterns in eastern North America. *Atmos. Environ.*, **22**:2751-2761.